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MODIFICATIONS OF WELL DEFINED POLYSILANES

by

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<p>Sonochemical synthesis of polysilanes provides polymers with low polydispersities and controlled molecular weights. Polysilanes which contain phenyl groups react with strong protonic acids such as triflic acid and form triflated polymers. Silyl triflates are strong electrophilic species and react with alcohols and amines. Polymeric triflates react in the same way leading to alkoxy and amino substituted polysilanes.</p>					
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Modifications of Well Defined Polysilanes

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Abstract

Different homo and copolysilanes are prepared using sonochemical reductive coupling of disubstituted dichlorosilanes with sodium. Polymers formed in the presence of ultrasound are monomodal and can have polydispersity as low as $\bar{M}_w/\bar{M}_n < 1.2$. Polysilanes containing aryl groups are dearylated upon treatment with strong protonic acids such as triflic acid. The resulting triflated polysilanes react readily with different nucleophiles providing alkoxy and amino substituted polysilanes. Triflated polymers react with monomers which can be polymerized cationically and form graft copolymers.

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1. Introduction

High molecular weight polymers which contain Si-Si bonds in the main chain have been known for more than thirty years but due to the insolubility of the initially prepared poly(dimethylsilylene) they were not studied in detail until recently¹. The successful conversion of poly(dimethylsilylene) to silicon carbide fibers and the subsequent preparation of soluble polysilanes gave rise to new studies of these materials. Photochemical and photophysical studies of high molecular weight polysilanes confirmed earlier theoretical predictions concerning conjugation of the catenated Si-Si bonds in linear polymers². Very recently thermochromism of polysilanes with long alkyl substituents has been observed and explained by the preferential formation of long (involving at least 10 consecutive Si atoms) "all trans" conformations.

Polysilanes are prepared by the reductive coupling of dichlorosilanes in the presence of sodium¹. The coupling process used at above 100°C leads usually to a mixture of high polymer ($\bar{M}_n > 100,000$), low polymer ($\bar{M}_n < 3,000$), and small cyclopolysilanes (Si₅ and Si₆). We have obtained monomodal polysilanes (only high polymers) by the application of ultrasound at ambient temperatures³.

The severe reaction conditions of the coupling reaction forbid applications of dichlorosilanes with substituents other than alkyl and aryl. Therefore up to now the availability of polysilanes was limited to polymers with alkyl or aryl substituents¹. We have recently discovered rapid and quantitative displacement of phenyl groups from silanes and disilanes by the action of strong protonic acids such as triflic acid⁴. The resulting triflates react rapidly with different nucleophilic reagents providing polysilanes with pendant alkoxy and amino groups. The reactivity of silyl triflates is sufficient

to initiate cationic polymerization of different monomers. The polymeric initiation system yields comb-like graft copolymers.

2. Sonochemical Synthesis of Well-Defined Polysilanes

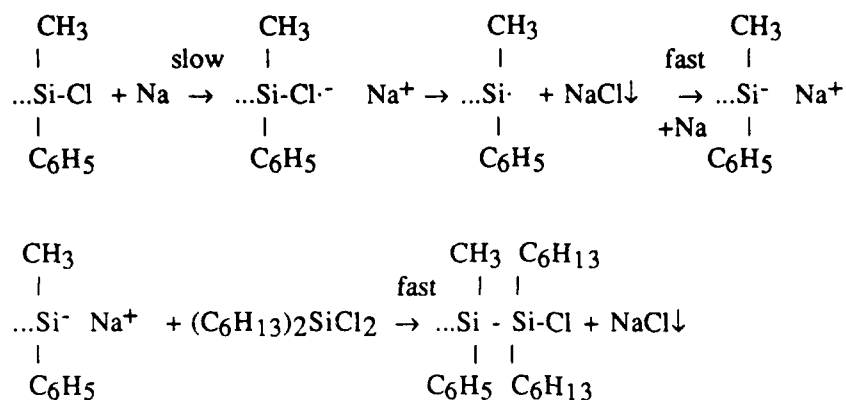
Ultrasound has recently been very successful in the application to different organometallic and catalytic reactions⁵. Rates are strongly accelerated and reactions are often much more selective than under typical thermal conditions. Sonication of sterically hindered dichlorosilanes in the presence of lithium yields disilenes and cyclotrisilanes⁶. We have applied ultrasound in the synthesis of poly(phenylmethylsilylene) in the presence of sodium dispersion which was prepared directly from small pieces of sodium by sonication.

Thermal polymerization typically results in the formation of high and low molecular weight polymer with a bimodal distribution. Bimodality was previously ascribed to the diffusional phenomena but an alternative explanation can involve the presence of two (or more) chain carriers which exchange slowly enough to build an entire macromolecule, or to the presence of linear and macrocyclic polymers. We expected that a lower overall temperature could favor one mechanism of propagation and yield monomodal polymers. Indeed, at ambient temperatures using simple cleaning baths or an immersion type probe we obtained monomodal poly(phenylmethylsilylene) with molecular weights in the range of $\bar{M}_n=100,000$ and polydispersities lower than $\bar{M}_w/\bar{M}_n < 1.3$.

Three phenomena may be related to the formation of monomodal polymers. The first one is the preferential contribution of intermediates of one type in the sonochemical reductive coupling. The second one accounts for the formation of high quality sodium dispersion which is continuously

regenerated during the coupling process. The third phenomenon is related to the selective degradation of polysilanes with higher molecular weights.

Sonochemical homopolymerization of dichlorosilanes is successful at ambient temperatures in nonpolar aromatic solvents (toluene, xylenes) only for monomers with α -aryl substituents. Dialkyldichlorosilanes do not react with sodium dispersion under these conditions but they can be copolymerized with phenylmethyldichlorosilane. Copolymers with 30 to 45% content of dialkylsilanes were formed from equimolar mixtures of the corresponding comonomers. Copolymerization might indicate anionic intermediates. A chloroterminated chain end in the polymerization of phenylmethyldichlorosilane can participate in a two electron transfer process with sodium (or rather two subsequent steps separated by a low energy barrier). The resulting silyl anion can react with both dichlorosilanes. The presence of a phenyl group in either α - or β -position in chloro terminated polysilane allows the reductive coupling in contrast to peralkyl species. Therefore, dialkyl monomers can copolymerize but they cannot homopolymerize under sonochemical conditions. The growth via radical intermediates should lead to the homopolymer of phenylmethylsilane in the presence of unreacted dialkyldichlorosilane unless extensive transfer process would operate. Radicals can be considered as intermediates which rapidly participate in the second electron transfer which leads to the corresponding anions. High local temperatures ($> 2,000$ °K) might enable the second electron transfer in spite of a short life time of active sites (≈ 1 μ s)⁵. Anions can react with both monomeric dichlorides in a S_N2 type reaction providing a copolymer:



The presence of the intermediate radicals was confirmed by trapping the pendant alkenyl groups in the polymerization of hexenylmethyl- and phenylhexenyldichlorosilane. In the reductive coupling of the latter monomer approximately 25% of alkenyl groups have been consumed but a small amount (<2%) of high polymer ($\bar{M}_n > 100,000$) has also been found. Growing anions have been detected by the additions of the deuterated protonic acids which led to the formation of Si-D bonds ⁷.

The reductive coupling must start at the slow reaction between sodium and monomer and is followed by much faster reactions involving polymeric species. Otherwise, no high polymer could be formed at the excess of sodium. The macromolecular silyl chloride should react with sodium in a two electron transfer reaction to form silyl anion. This anion will react faster with more electrophilic dichlorosilane than with a macromolecular silyl chloride. Thus, polymerization would resemble a chain growth process with a slow initiation and a rapid two-step propagation (the first step is the reaction of an anion with a monomer, the second is the reduction of a chloride to the anion).

Dialkyldichlorosilanes do not participate in the reductive coupling with sodium at temperatures below 60°C due to either thermodynamic or kinetic reasons. It might happen that the equilibrium constant for the reduction

process is unfavorably shifted at lower temperatures. Dialkylchlorosilanes could be polymerized at ambient temperatures in etheral solvents ⁸. For example, we prepared poly(di-n-hexylsilylene) with molecular weight $\bar{M}_n=45,000$ in mixtures toluene : diglyme (1:1). The presence of diglyme may accelerate electron transfer but it may also shift the equilibrium by the formation of complexes with sodium cations (cf. Table 1).

The active surface of sodium dispersion increases under ultrasonication. This has the origin in the cavitation erosion of sodium malleable at this temperature. The ultrasound also assures local excess of sodium by the continuous regeneration of the metal surface.

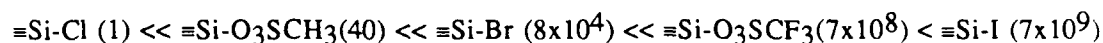
We have found that high molecular weight polysilanes are rapidly degraded in the presence of ultrasound (cf. Table 2). Similar effect has been observed previously for polystyrene, poly(methylmethacrylate), dextran, and other polymers ⁹. Selective degradation is of a mechanical nature caused by friction forces between macromolecules and solvent molecules during the cavitation process. Larger molecules are more resistant to flow, have larger shear forces, and rupture more frequently than shorter macromolecules. Beyond a certain molecular weight shear forces are smaller than bond strengths and polymers cannot degrade. This selective degradation reduces molecular weights to a certain value but also decreases polydispersity.

3. Model Dearylation Reactions

Successful polymer analogous reactions should proceed with high rates and high selectivities to enable reactions with functional groups which are usually present at low concentrations. Having in mind this limitation, we were searching for a rapid and selective reaction which could convert relatively inert silicon alkyl or aryl groups into intermediates capable of incorporation

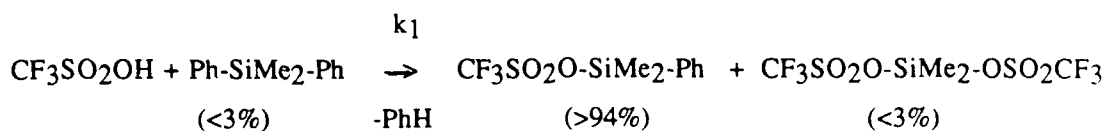
of different functionalities. Reductive coupling in the presence of alkali metal allows only alkyl and aryl groups at silicon. Alkoxy, amino groups, and even hydrogen atoms react rapidly with molten sodium leading to crosslinking and other side reactions.

On the other hand it is known that some electrophilic silyl compounds react rapidly with a large variety of nucleophiles. The relative order of reactivity of silylating reagents has been established in studies of silylation of cyclic and linear ketones¹⁰:



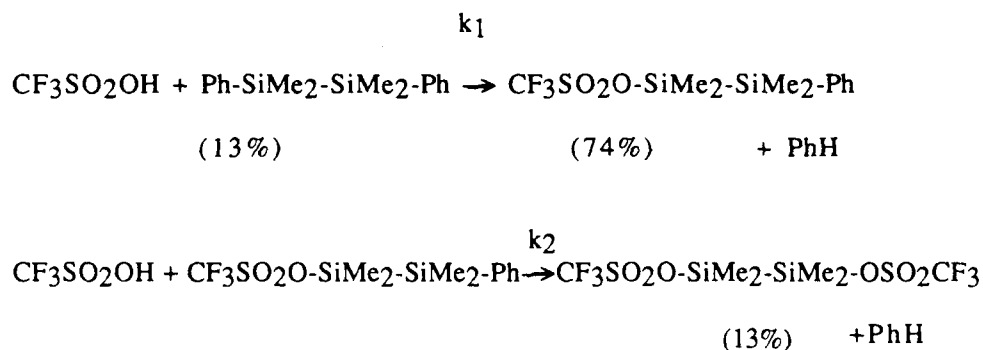
There is also some qualitative information that perchlorates might be more reactive than iodides¹¹. Thus, three silylating compounds are much more reactive than the others: iodide, perchlorate, and triflate. The first two have considerable disadvantages as light sensitive and explosive reagents, respectively. Whereas triflates are stable for a long time in the absence of nucleophiles (moisture included).

There are four synthetic routes leading to silyl triflates: reaction of silyl chlorides with silver triflate (very expensive), silyl chlorides with triflic acid, tetraalkylsilanes with the acid, and arylsilanes with the acid¹¹⁻¹³. The displacement of a chlorine atom and a phenyl group from trimethylsilylchloride and trimethylphenylsilane indicate that these groups are much more reactive than alkyl substituents in the synthesis of triflated silanes. We found that the aryl group is over 200 times more reactive than chloride in these reactions. We were able to displace two phenyl groups from diphenyldimethylsilane in a stepwise manner:



Phenyldimethyltrifluoromethanesulfonyloxysilane was formed after the reaction with one equivalent of the acid, and the corresponding ditriflate was formed after the second equivalent of the acid was added. No ditriflate was found until the starting material was completely consumed.

A similar reaction with 1,2-diphenyltetramethyldisilane shows a much lower selectivity. Reaction with the equimolar amount of the acid results in 13% of the starting disilane, 13% of ditriflate, and 74% of monotriflate:

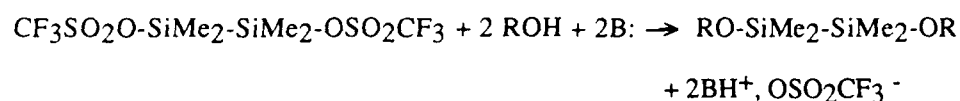


These results indicate that the second rate constant is approximately 8 times lower than the first one or, taking into account a statistical factor, the phenyl group is 4 times less reactive when a strong electron withdrawing triflate group is at the adjacent silicon atom. The presence of triflate at the same Si atom leads to much larger differences in reactivities and to a stepwise dearylation*.

* We prefer to use the term "dearylation", although in organosilicon chemistry desilylation is used, because in the polymeric systems we remove a large number of aryl groups and the silicon backbone (polysilane) remains intact.

1,2-Bis(trifluoromethanesulfonyloxy)tetramethyldisilane is formed in preparative yields which exceed 75%. The reaction between two equivalents of the acid and disilane shows only one desired product when carried out directly in an NMR tube.

The ditriflates react rapidly with different nucleophiles such as alcohols, amines, and organometallics:



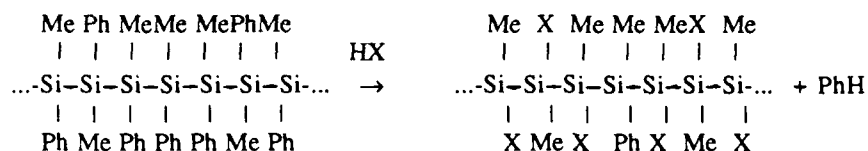
R = CH₃-, C₂H₅-, (CH₃)₃C-, CH₂=CH-CH₂-, CF₃CH₂- ,

We also observed quantitative reactions with other nucleophiles such as amines and organometallics.

4. Reactions on Polymers

Rapid and quantitative displacement of phenyl groups from model silanes suggests that similar reactions with aryl substituted polysilanes should lead to the triflated polymer. We have carried out this displacement under different conditions and we have found that approximately the first 80% of the phenyl groups are removed from poly(phenylmethyldisilylene) quite rapidly. No free acid was observed in the NMR spectra 2 minutes after addition of the acid. Later displacement becomes more difficult, and a small amount of phenyl groups (less than 10%) remains in the presence of excess acid. This is shown in Fig. 1. The broad signals of the starting material are due to the differences in the chemical shifts of phenyl and methyl groups in isotactic, syndiotactic, and atactic triads. Tacticity remains in a partially triflated polymer in which methyl groups being in the neighborhood of strong electron withdrawing

triflate moieties are strongly deshielded. A small amount of unreacted phenyl groups can be ascribed to some syndiotactic triads in which a phenyl group is placed between two bulky triflate groups and the steric hindrances prevent the displacement of the final aryl group:



(very slow, steric hindrance)

Strong electrophilic reagents can induce dearylation but they can also decrease molecular weights of polysilanes by cleavage of Si-Si bonds. We have found that the selectivity of dearylation in CH_2Cl_2 solutions using triflic acid is above 90% but at higher degrees of modifications we also observe degradation of a polymer. Thus, under present conditions dearylation using triflic acid is best suited for partial modifications and attachment of groups which can influence the physical and chemical properties of polysilanes even with a low content of these groups.

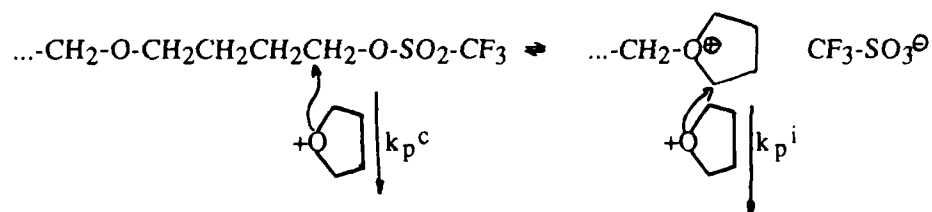
It has been found that polymers which contain 10 to 30% of methoxy, ethoxy, or tert-butoxy groups instead of phenyl groups have lower absorption maxima than the initial polymer (310 nm vs. 340 nm). This can be ascribed to the decrease of $\sigma \Pi^*$ excitation in the modified polymer¹⁴.

At present we are studying the optimal conditions of the displacement reactions by using different solvents, temperatures, and various acids. We have found that variation in the aryl groups also increases the selectivity of dearylation. For example, p-methoxyphenyl group is displaced by triflic acid much more rapidly than the unsubstituted phenyl ring.

5. Grafting from Polysilanes

It has recently been reported that trimethylsilyl triflate can initiate cationic polymerization of different vinyl and heterocyclic monomers¹⁵. The triflated polysilane can react in the same way and can produce growth of a large number of chains. In this way comb-like graft copolymers can be prepared.

Successful preparation of pure graft copolymer requires a transferless process, otherwise in addition to the desired graft copolymer a mixture of homopolymers will also be formed. The correct control of the structure of the graft copolymer can be achieved in the living system when initiation is of a rate higher (or comparative) than propagation and when termination is absent. There is a few monomers which can be polymerized cationically in living systems¹⁶. For example, cyclic ethers, cyclic iminoethers, and some cyclic amines give living systems. Recently some vinyl ethers were also polymerized in transferless and terminationless processes¹⁷. Quite often there are special requirements for the structure of the initiator. Triflate derivatives were successfully used in the living polymerization of cyclic ethers, particularly in the polymerization of tetrahydrofuran (THF)¹⁸. In the polymerization of THF in the presence of an anion capable of covalent bonding there are two types of active species: oxonium ions and covalent esters. They isomerize with rates comparable to the rate of propagation and the equilibrium position depends on the polarity of solvent:



Polymerization proceeds predominantly with ionic species because they are more than 1000 times more reactive than esters. Rapid isomerization allows simultaneous growth on all chains. Typically, in polymerization of THF polydispersities are above $\overline{M}_w/\overline{M}_n > 1.5$ since depropagation occurs simultaneously with chain growth. The equilibrium monomer concentration at room temperature is in the range of $[M]_e = 5 \text{ mol/L}$. Thus, the initial concentration of THF under these conditions must exceed 50 vol%.

We succeeded in grafting polytetrahydrofuran on partially triflated poly(phenylmethylsilylene) in CH_2Cl_2 . Using a polysilane with $\overline{M}_n = 3,600$ in which 30% of phenyl groups were substituted by triflates (9 groups per chain) we observed formation of a graft copolymer with $\overline{M}_w = 600,000$ and $\overline{M}_n = 300,000$. After UV irradiation the molecular weight of this polymer decreased to $\overline{M}_n = 30,000$. This suggests that polytetrahydrofuran was successfully grafted onto polysilane and that the amount of homopolytetrahydrofuran which could be formed by transfer or via direct initiation by the remaining triflic acid is very small.

The grafting process will be attempted for other monomers and for different counterions. The synthesis of true graft copolymers may lead to the formation of new morphologies if the size of components in the copolymer allows correct microphase separation. These studies are being continued in our laboratory.

Experimental

Details of this work have been described in References 3 and 4. All reagents were distilled and dried directly before use. Reactions were carried out either in inert atmosphere or using a vacuum line. NMR spectra were

recorded using 300 MHz and 80 MHz machines. GPC analysis were performed using ultrastyrigel columns (Waters).

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Caption for Figure 1

^1H NMR spectra of poly(phenylmethylsilylene) modified by trifluoromethanesulfonic acid (HA). (a) $[-\text{SiPhMe-}]_0 = 0.42 \text{ mol/L}$; (b) after reaction with $[\text{HA}]_0 = 0.17 \text{ mol/L}$; (c) after reaction with $[\text{HA}]_0 = 0.34 \text{ mol/L}$. CH_2Cl_2 as internal standard (5.35 ppm), CDCl_3 solvent, 25°C .

Table 1

Results of the Sonochemical Synthesis of Different Polysilylenes.

Monomer	PhMeSiCl ₂	PhMeSiCl ₂	PhMeSiCl ₂	PhMeSiCl ₂ (nHex) ₂ SiCl ₂	PhMeSiCl ₂ (nHex) ₂ SiCl ₂	PhMeSiCl ₂ + (nHex) ₂ SiCl ₂ (1:1)
Solvent	PhCH ₃ ⁺	PhCH ₃	PhCH ₃ [#]	PhCH ₃	PhCH ₃ (+25% diglyme)	PhCH ₃
0C	110	60	40	60	60	60
% polymer	55	12	11.1	0	24	12
HP/LP	1/3(1/9)	1/0	1/0	-	1/0	1/0*
M _n @·10 ⁻⁵ (HP)	1.07	1.04	1.3	-	0.45	1.75
M _n ·10 ⁻³ (LP)	3.3	-	-	-	-	-
M _w /M _n	1.81	1.5	1.20	-	1.73	1.66

[M]₀ = 0.32 mol/L, toluene, [Na]/[M]₀ = 1.2Reaction time: 60 min (thermal⁺ and immersion), 180 min (cleaning bath #)* Ratio [PhMeSi]/[(nHex)₂Si] in a copolymer was 1.5/1.0

@ Molecular weights are based on polystyrene standards, vpo and light scattering measurements indicate that "true" molecular weights of polysilanes are approximately two times larger.

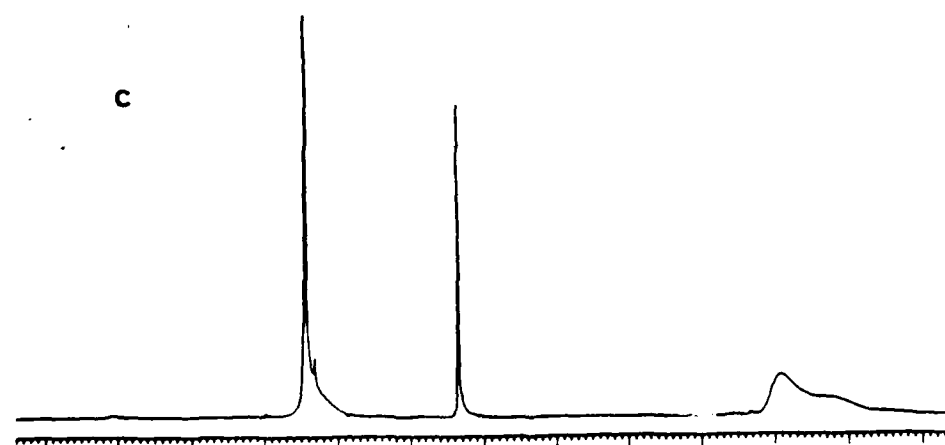
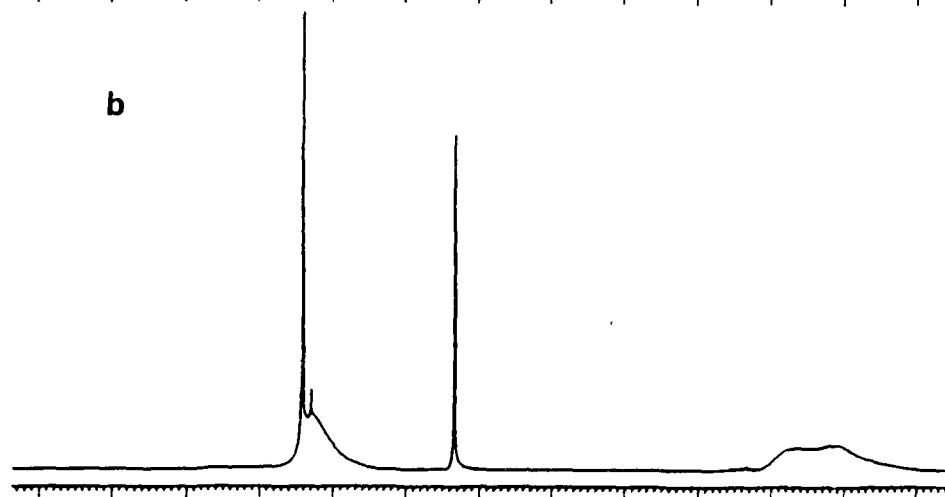
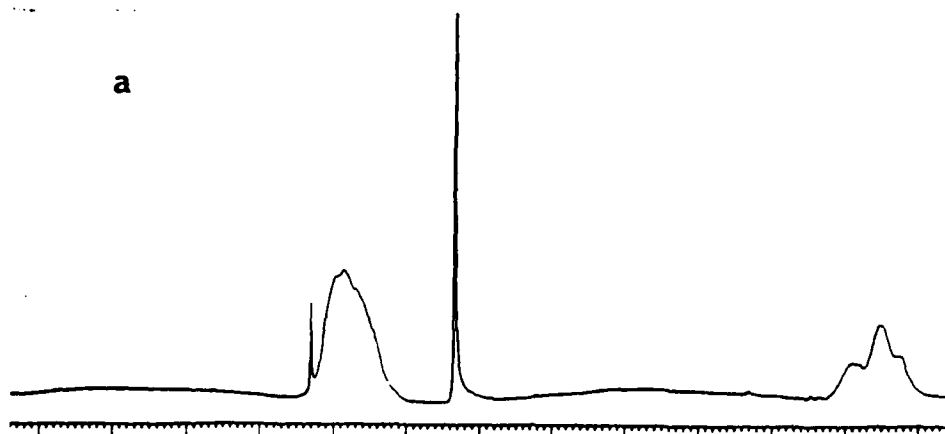
Table 2

Effect of Sonication Time on Molecular Weights and Polydispersities of Poly(phenylmethylsilylene)

	During Addition					After Addition				
	time min	5	10	15	11	30	60	80	120	
$M_n \cdot 10^{-5}$		3.8	2.24	2.30		1.82	1.48	1.06	0.40	
$M_w \cdot 10^{-5}$		17.3	6.68	6.35		3.73	2.57	1.57	0.47	
M_w/M_n		4.5	2.98	2.71		2.05	1.73	1.48	1.17	

[PhMeSiCl₂]₀ = 0.32 mol/L, toluene, [Na]₀/[Si-Cl]₀ = 1.2

T = 60 °C, Immersion Type Probe



101, 102